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Equilibrium partial pressure of CO_2 in the Callovo-Oxfordian argillite as a function of relative humidity

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Abstract

Understanding the behavior of a clay mineral-rich rock submitted to different physical-chemical perturbations is important for assessing the safety of nuclear waste disposal facilities in the corresponding geological formations. In this work we studied the effect of rock desaturation on the CO_2 partial pressure signature of the Callovo-Oxfordian argillite. This integrated study, which combines experiments and geochemical modeling, points out the primary role of capillary forces on the chemical equilibria. In particular, it was possible to model, without any fitting parameters, the experimental decrease of pCO_2 as a function of decreasing water content in the argillite. Moreover, this application to a complex natural system is an example of confirmation of the theoretical concepts of geochemistry in capillary contexts and is promising for dealing with other natural and industrial systems.

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Keywords: nuclear waste storage, Callovo-Oxfordian argilite, capillary systems, relative humidity, isobar/anisobar contexts, carbon dioxide, geochemical modeling.

1. Introduction

During the building and utilization of a nuclear waste repository in a clayrock geological formation, the rock should desaturate around the galleries. Consequences of such a perturbation must be assessed to predict the evolution of water composition that will interact with repository materials. In the present

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work, we focus on the geochemical aspect of this perturbation by means of an integrated approach combining experiments and numerical simulations.
One of the main particularities of the system under consideration is that the decreasing water content in the rock generates capillary constraints, *i.e.* negative pressures in the pore water [1]. Recently, experimental evidence of changes in reactivity of simple systems due to capillary constraints has been obtained [2]. Theoretical calculations have also been carried out which show that gases in capillary pore water should have an increased solubility relative to bulk free water [3], because of the pressure-induced changes in the thermodynamic properties of water and dissolved species [4].
The purpose of the present work is to determine whether such phenomena do occur and, if so, whether they can be described in the more complex case of the Callovo-Oxfordian (COx) argilite understudy as the proposed host formation for installation of a future French Radioactive waste repository.

2. Materials and methods

The COx sample (taken from the EST 312 borehole) has been coarsely crushed followed by separation of the 5 to 8 mm size fraction. The aim of this crushing operation is to maximize the surface area without changing the pore characteristics of the argillite. The samples were then fully hydrated by contacting with synthetic COx porewater over a period of 3 months.
Experiments were conducted at ambient temperature in sealed bombs filled with about 200 g of hydrated sample. The bombs were initially flushed with a mixture of dry Argon and water vapor to give initial relative humidities (RH) of 50, 68, 95, and 100%. The total pressure (> 1 bar), temperature, CO_2 partial pressure (pCO_2) and RH of each system were monitored throughout the experiment. Temperature remained almost constant for each sample (T~25°C). The pCO_2 was measured by gas chromatography, and RH with a hygrometric sensor.

3. Theoretical background

3.1. Geochemical model for the Cox argillite

The geochemical description of the COx is done using the alternative model #1 of Gaucher *et al.* [5]. In addition to the mineralogical and cation exchange control of the solution included in this model, we added the protonation/deprotonation surface complexation model of Bradbury and Baeyens [6,7] in order to take the pH buffering capacity of the lateral surfaces of clay minerals into account.

According to literature data [8], we consider a total amount of 15 g of water in 200 g of water-saturated COx. The amount of pore water remaining in the rock samples at various relative humidity (RH) values was then deduced from the hydration isotherm given in [8]. This evaporation process is implemented in the modeling so that its impact on the chemical composition of the pore solution is considered. In particular, the increasing ionic strength with decreasing water content is taken into account.

3.2. Thermodynamics of chemical reactivity in capillary systems

The chemical behavior of capillary systems has been studied for more than ten years, and the theoretical framework is now well established for calculating the standard thermodynamic properties of chemical compounds submitted to capillary pressure [1,3,4]. Capillary systems offer specific features called the anisobar contexts (*i.e.*, where phases can undergo different pressures). They apply particularly to gas-solution equilibria since a gaseous compound cannot undergo negative pressures whereas its aqueous equivalent undergoes the internal capillary water pressure. A similar situation can be envisioned for minerals initially present in the rock matrix. They are submitted to the local pressure constraint when

the porosity is saturated with water and the same pressure applies to these minerals during desaturation regardless of water content. On the other hand, if the capillary aqueous solution is supersaturated with respect to a mineral, the latter should precipitate at the capillary water pressure. Some evidence for this isobar/anisobar situation was obtained experimentally [2].

Moreover, as aqueous species are impacted by capillary pressure, we infer that cation exchange constants should also be affected. This is implemented in this work assuming the anisobar configuration.

3.3. Thermodynamic database

We used the well-known PhreeqC-2 geochemical calculation code [11] for calculatingpCO_2 at equilibrium with the COx mineralogy and the pore water. The use of this code at temperatures and pressures different from the liquid-vapor saturation curve is possible if appropriately adapted thermodynamic databases are available. These were generated using the Thermo-ZNS code [3] and include both isobar and anisobar mineral dissolution/precipitation reactions. The reference thermodynamic database implemented in Thermo-ZNS is the Thermoddem database [12] that provides information on critically selected standard thermodynamic properties of chemical compounds and reactions necessary for their calculation at various temperatures and pressures.

4. Results and discussion

Fig. 1a indicates that pCO_2 reaches a constant value after 11,000 h of "water/rock/gas" interactions for the 100% RH experiment. Under these conditions, the equilibrium pCO_2 with the COx argillite equals 8.0 mbar, which is in good agreement with the theoretical value [5].

Measured pCO_2 as a function of relative humidity is plotted in Fig. 1b (closed squares). It shows that decreasing RH decreases pCO_2 at equilibrium with the clayrock. Calculated equilibrium pCO_2 are also plotted in Fig. 1b (curves). Calculations involve all geochemical contributions evoked in § 3.1. with (heavy line) or without (dashed line) the effect of capillary pressure on chemical equilibria. Better results are clearly obtained when considering capillary pressure. The decrease of pCO_2 with RH, indicated by the dashed line (Fig. 1b), is due to the increase of ionic strength in the pore solution resulting from evaporation of water and is in accordance with the salting-out effect. However it is not sufficient to explain the experimental measurements. The simple introduction of the capillary constraints shifts the (heavy line) curve so that it closely fits experimental data. As expected, there is no difference between the two calculations at saturation, and discrepancies increase as RH decreases. In both series of calculations, pH is buffered between 7.13 and 7.15 as a result of the protonation /deprotonation surface reactions.

One of the main features is the isobar/anisobar behavior of minerals. Anisobar minerals are destabilized by capillary pressure. They partly dissolve in favor of the isobar polymorphs that are stabilized and can therefore precipitate. Given the duration of the experiments, only supposedly reactive minerals were allowed to re-precipitate, namely calcite, celestite, and chalcedony (if possible after anisobar quartz has dissolved). Other minerals initially present (illite, chlorite, and pyrite) were only allowed to dissolve. These mass transfers, combined with aqueous speciation and CO_2 solubility variations, all contribute in a consistent fashion to the calculated equilibrium pCO_2.

5. Concluding remarks

The experimental results obtained in this study were reproduced by calculation without any parameter adjustment. This strongly supports the theoretical principles of chemistry in capillary contexts and is encouraging for extending its application to other natural and industrial systems where capillary

phenomena may occur, namely in finely porous systems subject to drying. Moreover, since the amounts of water are generally limited in such systems, it is worth pointing out that their effective impacts may be most probably observable over long timeframes.

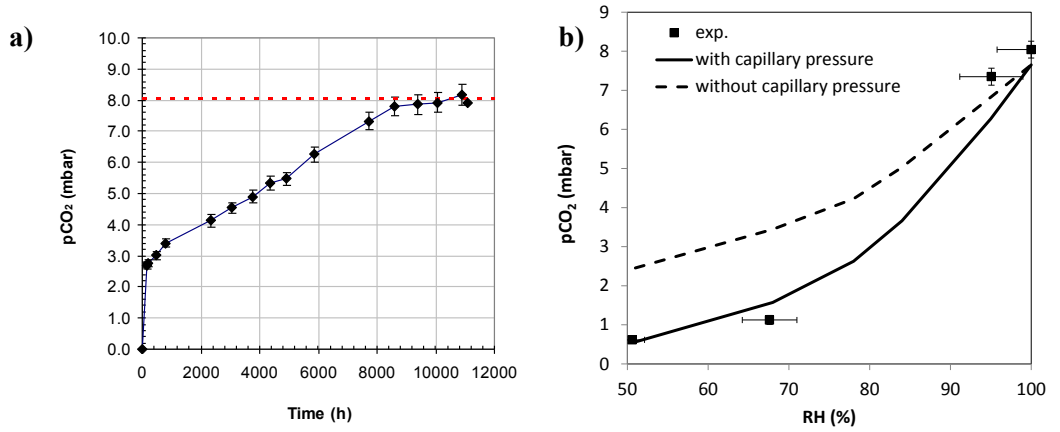

Fig. 1. (a) Evolution with time of pCO_2, for the 100% RH experiment. The red dashed-line represents pCO_2 supposedly at equilibrium with the COx. (b) pCO_2 at equilibrium with the COx as a function of RH. Closed squares: experimental data, heavy line: numerical model including capillary constraints, dashed line: numerical model without capillary constraints.

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